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<b>(21) International Application Number:</b> PCT/DK96/00525 <b>(22) International Filing Date:</b> 12 December 1996 (12.12.96) <b>(30) Priority Data:</b> 1468/95 22 December 1995 (22.12.95) DK <b>(71) Applicant (for all designated States except US):</b> DANSK TEKNOLOGISK INSTITUT [DK/DK]; Gregersensvej, P.O. Box 141, DK-2630 Taastrup (DK). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> KRÆMER, Ole [DK/DK]; Gadeledsvej 92, DK-3400 Hillerød (DK). SCHMIDT, Mar- ianne [DK/DK]; Johannevej 3, DK-2740 Skovlunde (DK). <b>(74) Agent:</b> HOFMAN-BANG & BOUTARD, LEHMANN & REE A/S; Hans Bekkevolds Allé 7, DK-2900 Hellerup (DK).	<b>(81) Designated States:</b> AL, AM, AT, AT (Utility model), AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, CZ (Utility model), DE, DE (Utility model), DK, DK (Utility model), EE, ES, FI, FI (Utility model), GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SK (Utility model), TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>In English translation (filed in Danish).</i>	
<b>(54) Title:</b> A METHOD OF MANUFACTURING IRON SHOT FOR HUNTING CARTRIDGES  <b>(57) Abstract</b>  A method of manufacturing iron shot, wherein essentially carbon free iron powder is compacted so as to form small bodies, and the small bodies formed are heated for a sufficient period to obtain partial sintering of the iron particles.		

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A method of manufacturing iron shot for hunting cartridges

The present invention relates to a method of manufacturing iron shot for hunting cartridges.

- 5 It has been known for long to use lead shot in hunting cartridges. Such lead shot are typically spherical and have a diameter which varies dependent on the type of game to be hunted. For example for hunting pheasants and other gamebirds, use is made of lead shot having a  
10 diameter of about 3 mm.

The known lead shot typically has a density of about 11.3 g/cm<sup>3</sup>.

- 15 Since lead is toxic to animals and human beings, and since, as a result of hunting, large quantities of shot are scattered annually throughout the countryside, steps have been taken during recent years to limit, and on a longer view, stop the use of lead shot.

Attempts have been made to replace lead shot by shot made from various lead-containing mixtures.

- 20 Thus, it is known from US patent specification No. 3,900,317 to replace lead shot by composite shot made from mixtures of particles of lead, iron, tin and zinc, which after agglomeration so as to form spherical bodies are sintered at a temperature of about 940 °C.

- 25 US 3,987,730 also describes composite shot consisting of iron, lead, tin and zinc. These known shot consist of an iron phase which may be in the form of a porous matrix, the voids of which are filled with lead or a lead-containing alloy which imparts a density of as much as 11  
30 g/cm<sup>3</sup> to the shot.

DE-OS-2,453,881 describes a method of manufacturing iron shot having sufficiently high strength to be used for hunting purposes, and which do not cause undue wear on the gun barrel. According to the method conventionally  
5 manufactured iron shot are subjected to a heat treatment at a temperature of 593-982 °C in a reducing atmosphere in order to remove carbon from the surface of the iron shot.

US-A-2,284,638 describes a method of manufacturing  
10 hardenable metal bodies by compacting a mixture of iron powder and iron carbide powder so as to form a coherent body, this body subsequently being heated in a non-oxidizing atmosphere for a sufficient period to obtain sintering of the iron powder particles and diffusion of  
15 iron carbide into the mass thus formed, whereby the latter becomes hardenable.

It has also been suggested to use steel shot as a substitute for lead shot. Such steel shot have a comparatively high degree of hardness, which causes  
20 considerable problems.

In case of woodland hunting, some of the shot end up in tree trunks, and when these trunks are subsequently cut, e.g. into veneer, the hard steel shot may cause damage to or destruction of the knives used for the cutting. This  
25 is an essential reason why although it is desired to abolish lead shot, it is still allowed to use lead shot for woodland hunting.

The object of the present invention is to provide non-toxic iron shot which do not destroy the tools used for  
30 wood-working, and which at the same time have satisfactory strength and penetration power to kill the game.

This object is achieved by the method according to the invention, which method is characterized in that essentially carbon free iron powder is compacted so as to form small bodies, and that the small bodies formed are  
5 heated for a sufficient period to obtain partial sintering of the iron particles.

The iron shot prepared by the method according to the invention have sufficiently high strength to kill the game without fracturing, and at the same time such  
10 brittleness that they disintegrate upon contact with hard objects or surfaces. Such disintegration thus occurs if, having penetrated into wood which is to be cut, they are hit by a veneer knife. The same applies if the shot strike hard road surfaces, ice-covered surfaces, or the  
15 like. Hereby the problems of ricocheting, which may arise when using conventional steel shot, are reduced.

The iron powder used in the method according to the invention preferably has a high degree of purity and contains only very small amounts of iron oxides. The  
20 particle size is preferably within the range 0.01-0.5 mm.

In connection with the compacting of the iron powder it is preferably admixed with lubricant in order to reduce the friction between the powder particles and the tool. Hereby also good green strength is obtained.

25 According to a preferred embodiment of the method according to the invention, the iron powder is compacted so as to form small bodies having larger dimensions than the desired shot, and the small bodies are abraded either before or after the sintering so as to obtain shot having  
30 a desired form and size.

The compacting is expediently performed by means of such matrices that oblong bodies with rounded ends and

circular cross-section are formed. When manufacturing approximately spherical shot having a diameter of 3 mm, the said oblong bodies preferably have a length of about 3.5 mm and a diameter of about 3.2 mm.

- 5 The compacting of the iron powder is typically performed using pressures between 200 and 600 MPa and results in a deformation of the iron powder particles.

As appears from the drawing, which shows an enlarged cross-sectional view of an iron shot manufactured by the  
10 method according to the invention, the compacting of the iron particles has resulted in their surfaces having adapted themselves to one another, whereby the void between the particles has been reduced to a minimum.

By using powder of essentially pure iron, the partial  
15 sintering of the iron particles is preferably performed at a temperature of 700-810 °C, and particularly expediently at a temperature of about 790 °C. The sintering is preferably performed in a reducing atmosphere, e.g. hydrogen-containing atmosphere, in order to obtain a  
20 reduction of any iron oxides. The partial sintering serves to establish punctiform bonds between the deformed iron particles.

These punctiform bonds have limited strength, which contributes to the shot, when exposed to strong  
25 mechanical impacts, fracturing at the interfaces between the deformed iron particles.

The above temperature is typically maintained for 20-30 minutes, whereafter the compacted small bodies have obtained suitably high strength following cooling to room  
30 temperature.

During the heating to a temperature within the above range, any lubricating and/or binding agents will evaporate or decompose, so that the sintered bodies obtained essentially consist only of iron.

- 5 The iron powder used can be admixed with small amounts of one or more additives, such as ferrophosphorus, manganese sulphide, tin and graphite, with a view to changing its sintering temperature, workability etc. In this case it may be a possibility to perform the partial sintering  
10 within a temperature range outside the range stated above. Any additives are preferably used in an amount of maximally 5 weight-%.

- The abrasion of the small bodies formed at the sintering, so as to obtain shot having a desired form and size, is  
15 expediently performed by placing the small bodies in a container equipped with a paddle-wheel agitator and containing a suspension of an abrasive, such as aluminium oxide or silicon carbide. During the movement caused by such an agitator, e.g. oblong small bodies or irregularly  
20 shaped small bodies will in time become essentially spherical.

- The density of the shot prepared by the method according to the invention is about  $7 \text{ g/cm}^3$ , which density combined with the strength of the shot has been found to give  
25 satisfactory penetration power.

- Following prolonged stay in live wood, the shot manufactured by the method according to the invention may tend to discolour the wood. In order to counteract or eliminate such tendency to discoloration, the shot are  
30 preferably subjected to a surface treatment so as to provide a surface coating on the shot. The surface treatment may e.g. be hot-dip galvanization, zinc

electroplating, tinning, or another kind of environmentally acceptable surface treatment.

The invention is described in more detail below, reference being made to the following examples.

5    Example 1

As starting material use is made of commercially available iron powder having good flow properties and a grain size of about 0.2 mm. About 0.5 weight-% of a lubricant consisting of 70 % zinc stearate and 30 % wax was added  
10    to the powder.

The iron powder and the lubricant were mixed in a V-mixer with internal rotor. The mixing time was about 25 minutes for a batch of 4 kg.

The powder was cooled to room temperature, whereafter it  
15    was ready for compacting.

The compacting was performed using a press comprising a top and a bottom piston at a pressure of about 500 MPa.

The bodies formed at the compacting had the shape of cylinders with rounded ends. The diameter of the  
20    cylinder-shaped portion of the compacted bodies was about 3.2 mm, and the length of the bodies was about 3.5 mm.

The compacted bodies, which had a density of about 7.3 g/cm<sup>3</sup>, were subsequently abraded so as to obtain essentially spherical shot having a diameter of about 3  
25    mm by making them roll against each other in a container equipped with an agitator and containing an aqueous suspension of fine-grained aluminium oxide. The container had a volume of 5 litres, and the quantity of compacted bodies was about 300 g per portion, which were treated  
30    for about 20 minutes.



After the abrasion the bodies were cleaned with soap and water, and subsequently dried.

The bodies were subjected to a heat treatment in order to effect partial sintering of the iron powder particles.

- 5 The heat treatment took place in a throughflow furnace, in which the temperature at the inlet was 500 °C, and in which the highest temperature was 790 °C. The bodies were kept at a temperature of about 500 °C for 30 minutes, and subsequently at a temperature of 790 °C for another 30  
10 minutes. The sintering process was performed in a hydrogen atmosphere. The sintered bodies were subsequently cooled to room temperature for about 30 minutes.

- The iron shot prepared had a density of about 7.3 g/cm<sup>3</sup> and caused no damage to veneer knives when cutting. The  
15 shot remained intact after shooting against hard wood fibreboards and bones.

#### Example 2

The method according to example 1 was repeated, but using a compression pressure of 400 MPa.

- 20 The shot thus prepared had a density of 6.8-7.0 g/cm<sup>3</sup> and were more brittle than the iron shot prepared according to example 1. This manifested itself in that in shooting tests they disintegrated on impact with bones cast in a muscle-like gel.

#### 25 Comparative example

- The method according to example 1 was repeated, but using a maximum temperature of 850 °C. The iron shot hereby obtained, which had a density of 7.3 g/cm<sup>3</sup>, were so hard that when cutting the shot with veneer knives, the knives  
30 suffered damage.

C l a i m s :

1. A method of manufacturing iron shot, c h a r a c -  
t e r i z e d in that essentially carbon free iron  
powder is compacted so as to form small bodies, and that  
5 the small bodies formed are heated for a sufficient  
period to obtain partial sintering of the iron particles.
2. A method according to claim 1, c h a r a c t e r -  
i z e d in using iron powder having a particle size of  
0.01-0.5 mm.
- 10 3. A method according to claim 1 or 2, c h a r a c -  
t e r i z e d in that the compacting is performed at a  
pressure of 200-600 MPa.
4. A method according to any of the preceding claims,  
c h a r a c t e r i z e d in that the iron powder is  
15 compacted into small bodies having larger dimensions than  
the shot desired, and that the small bodies either before  
or after the sintering are abraded so as to obtain shot  
having a desired shape and size.
5. A method according to any of the preceding claims,  
20 c h a r a c t e r i z e d in that oblong small bodies  
with rounded ends and circular cross-section are formed  
at the compacting.
6. A method according to any of the preceding claims,  
comprising using a powder of essentially pure iron,  
25 c h a r a c t e r i z e d in that the sintering is  
performed at a temperature of 700 °C - 810 °C.
7. A method according to any of the preceding claims,  
c h a r a c t e r i z e d in that the iron powder is  
admixed with one or more additives before the compacting.

8. A method according to any of the preceding claims, characterized in that the sintering temperature is maintained for 20-30 minutes.
9. A method according to any of the preceding claims, characterized in that the sintering is performed in a reducing atmosphere.
10. A method according to any of the preceding claims, characterized in that the abrading of the small bodies is performed in a container equipped with an agitator and containing a suspension of a particle shaped abrasive agent.
11. A method according to claim 10, characterized in using aluminium oxide or silicon carbide as abrasive agent.
12. A method according to any of the preceding claims, characterized in that the finished shot are subjected to a surface treatment so as to provide a surface coating on the shot.
13. Iron shot manufactured by the method according to any of the claims 1-12.

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## INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 96/00525

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: F42B 7/04 // B22F 3/12

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: F42B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2284638 A1 (F.H. CLARK ET AL), 2 June 1942 (02.06.42) --	1
Y	DE 2453881 A1 (ARTHUR D. LITTLE, INC.), 19 June 1975 (19.06.75) --	1
A,P	EP 0718589 A1 (FIOCCHI MUNIZIONI SPA), 26 June 1996 (26.06.96) --	1
A	US 3987730 A (F.W. MEADUS ET AL), 26 October 1976 (26.10.76) -- -----	1

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

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Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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DE-A1- 2453881	19/06/75	FR-A- 2254646 SE-A- 7415597 US-A- 3874295	11/07/75 16/06/75 01/04/75
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